



SEP 3 1992

CONFIDENTIAL
ATTORNEY WORK-PRODUCT
COMMUNICATION

September 1, 1992
92C0094A

EPA Region 5 Records Ctr.



275066

David E. Northrop
Samuels and Northrop Co. LPA
180 East Broad Street, Suite 816
Columbus, Ohio 43215

Subject: Manganese Occurrence in Soil and Water at the Skinner Landfill

Dear Dave:

I have completed my review of the Phase II Remedial Investigation Report (May 1991), Baseline Risk Assessment (June 1991), and the Feasibility Study (April 1992) for the Skinner Landfill. This letter report provides a summary of the reported occurrence of manganese in soil and water at the Skinner Landfill and contains a brief review of the geochemistry of manganese as it pertains to the mobility of this metal in the environment. This report concludes with an evaluation of the fate of potassium permanganate (KMnO_4) in the landfill and the potential for permanganate to be a source of manganese in the soil and groundwater.

Introduction

At an industrial facility operated by Aeronca in Middletown, Ohio, a solution containing potassium permanganate as a cleaning agent was used in a cleaning bath. Spent solution was sent to the Skinner Landfill in West Chester, Ohio that has now become a CERCLA site. Woodward-Clyde Consultants has been retained to evaluate the fate of potassium permanganate in the landfill and the potential for the spent cleaning solution to be a source of manganese in the soil, groundwater or surface water in the vicinity of the landfill.

Occurrence of Manganese in Soil, Sediment and Water at the Skinner Landfill

The Remedial Investigation (RI) Report, Baseline Risk Assessment (BRA) and Feasibility Study (FS) of the Skinner Landfill prepared by WW Engineering & Science for EPA Region V were reviewed to evaluate the presence of manganese in the environmental media and determine if manganese has been considered by EPA to be a contaminant of concern in any of these media.

Woodward-Clyde Consultants

David E. Northrop
Samuels and Northrop Co. LPA
September 1, 1992
Page 2

Sixty-two soil samples were collected in the vicinity of the buried waste lagoon and analyzed for a wide variety of potential contaminants, including manganese. The range of detected manganese concentrations in soil near the waste lagoon is 168 to 2,430 mg/kg (RI Table 5.3). Seven soil samples were collected in the vicinity of the buried pit and analyzed for manganese. The range of detected manganese concentrations in soil near the buried pit is 639 to 3,630 mg/kg (RI Table 5.4). Nineteen additional soil samples were collected and analyzed for manganese from monitoring well boreholes throughout the site. The range of detected manganese concentrations from these samples is 337 to 1,830 mg/kg (RI Table 5.5). The range of background concentrations for manganese in soil has been reported as 542 to 1,180 mg/Kg (RI Tables 5.3, 5.4 and 5.5). Manganese is not considered a chemical of concern for soils based on a comparison with background levels (BRA Table 2-1).

Sediments from three creeks, three ponds and three leachate seeps were sampled. The range of manganese concentrations for the 32 sediment samples collected is 470 to 3,520 mg/Kg (RI Tables 5.13, 5.15, 5.17 and 5.19). The range of background concentrations for manganese in sediment has been reported as 805 to 3,250 mg/Kg (RI Tables 5.13, 5.15, 5.17 and 5.19). Manganese is not considered a chemical of concern for sediments based on a comparison with background levels (BRA Table 2-1).

Manganese was detected in 13 of 15 water samples collected from the unconsolidated sediment wells. The range of manganese concentrations is 0.0346 to 1.93 mg/L (RI Table 5.8). The range of background manganese concentrations for the unconsolidated sediment wells is 0.021 to 0.074 mg/L (RI Table 5.8). Manganese was detected in 14 water samples collected from the bedrock wells. The range of manganese concentrations is 0.016 to 1.43 mg/L (RI Table 5.9). The background manganese concentration for the bedrock wells is reported as 0.0719 mg/L (RI Table 5.9). [The secondary Maximum Contaminant Level for manganese in drinking water is 0.05 mg/L.] Based on a comparison of measured manganese concentrations in groundwater with background concentrations, manganese is considered a chemical of concern in the bedrock and unconsolidated sediment groundwater (BRA Table 2-1).

Surface water from three creeks, three ponds and three leachate seeps was sampled and analyzed during Phase II of the RI. Based on a comparison with background manganese concentrations, manganese is not considered a chemical of concern in surface water at any of these locations except Skinner Creek (BRA Table 2-1). The range of manganese concentrations for the surface water samples collected from Skinner Creek is 0.0163 to 0.0715 mg/Kg (RI Tables 5.14). The background manganese concentration for water in Skinner Creek is reported as 0.0094 mg/Kg (RI Table 5.14).

Woodward-Clyde Consultants

David E. Northrop
Samuels and Northrop Co. LPA
September 2, 1992
Page 3

In summary, manganese is not considered to be a chemical of concern in soils or sediments at the Skinner Landfill. Because it is elevated in concentration above background in bedrock and unconsolidated sediment groundwater and surface water in Skinner Creek, manganese is considered a chemical of concern for these media. The following section of this report discusses the geochemistry of manganese as it applies to the presence and mobility of manganese in the natural environment and under contaminant conditions.

Manganese Geochemistry

The geochemistry of manganese is complex because it occurs in three valence states Mn(II), Mn(III) and Mn(IV) under most natural environmental conditions. Potassium permanganate (KMnO_4) is an industrial product that is used as a strong oxidizing agent because manganese in permanganate is in the Mn(VII) valence state. Mn(VII) is unstable and, under appropriate conditions, will clean material by oxidation. In this reaction, manganese is reduced to a more stable, lower valence state. In solution under near neutral pH conditions, the dominant manganese species (Mn^{2+} and MnOH^+) are in the Mn(II) valence state.

As a consequence of the variety of valence states of manganese, the solubilities of manganese minerals are strongly affected by the oxidation/reduction (redox) state of the environment as well as the pH. For instance, in pure water under well oxidized conditions ($p_e = 9.62$, where p_e is the negative log of the activity of the electron) and a solution pH of 7, the solubilities, based on thermodynamic equilibrium calculations, of pyrolusite ($\beta\text{-MnO}_2$) and manganite ($\gamma\text{-MnOOH}$), both common soil minerals, are equal to about 0.25 mg/L. This is a common dissolved manganese concentration found in oxidized groundwater. If the p_e were lowered by 1 p_e unit to 8.62 (i.e., less oxidizing conditions), the solubility of pyrolusite would be 25 mg/L and the solubility of manganite would be 2.5 mg/L. Concentrations of manganese in groundwater in areas of organic contamination associated with landfills or leaking storage tanks are commonly in the range of 10 to 30 mg/L (Baedecker, M. and M.A. Apgar. 1984. Hydrogeochemical Studies at a Landfill in Delaware. Studies in Geophysics pp. 127-138). The reason for the elevated manganese concentrations in the groundwater is that the organic contaminants consume dissolved oxygen in the groundwater and produce local conditions that are reducing. This condition increases the solubility of the naturally occurring manganese minerals in the soil. The upper limit on dissolved manganese concentration under reducing conditions may be controlled by the formation of rhodochrosite (MnCO_3) which forms when $\text{CO}_2(\text{g})$ pressures are high (Lindsay, W.L. 1979. Chemical Equilibria in Soils, Wiley-Interscience, 449p.). A condition of high

Woodward-Clyde Consultants

David E. Northrop
Samuels and Northrop Co. LPA
September 1, 1992
Page 4

CO₂(g) pressure is also associated with the oxidation of organic contaminants in soil or groundwater.

Fate of Potassium Permanganate and Manganese at the Skinner Landfill

In the early years of operation of the Skinner property as a landfill, it was used to dispose of general municipal refuse (EPA Proposed Plan for Skinner Landfill, April 1992). As discussed above, the leachate produced by refuse in landfills produces reducing conditions that generally mobilize manganese in the subsoil below the landfill. This results in elevated manganese concentrations in water compared to normal oxidizing conditions of near surface groundwater. Organic solvents subsequently added to the landfill as industrial waste would tend to maintain the reducing conditions and keep manganese mobile. On the other hand, permanganate in the spent wash solution, being a strongly oxidizing compound, would tend to produce oxidizing conditions. Under oxidizing conditions and pH values measured for the unconsolidated sediment and bedrock groundwater (6.67 to 9.51, RI Table 5.6), manganese minerals are not very soluble, as discussed above, and it is rare to find dissolved manganese concentrations greater than 1 mg/L under these conditions. Under oxidizing conditions, the manganese in the permanganate will precipitate in the soil because potassium permanganate is not thermodynamically stable. The precipitation of a manganese mineral will provide a source of manganese in the soil, however natural soil is also a source of manganese as shown by the background soil manganese concentrations reported as 542 to 1,180 mg/Kg (RI Table 5.3). The organic contaminants at the site mobilize the manganese by producing reducing conditions.

Summary and Conclusions

Manganese is considered a chemical of concern only for the groundwater and Skinner Creek surface water at the Skinner Landfill site. The disposal of spent potassium permanganate cleaning solution to the landfill adds manganese to the environment; however, the geochemistry of manganese is such that permanganate will produce oxidizing conditions and form relatively insoluble manganese minerals. If oxidizing conditions are maintained, the dissolved manganese concentrations in groundwater and surface water should not be elevated relative to background. The mechanism for mobilizing manganese at the Skinner Landfill is the reducing conditions created by the organic material in the waste disposal areas. Under reducing conditions, oxidized manganese minerals are soluble. Oxidized manganese minerals are common in soil and probably account for the measured manganese concentrations in background soil samples. The actual source of elevated dissolved manganese found in the groundwater

**Woodward-Clyde
Consultants**

David E. Northrop
Samuels and Northrop Co. LPA
September 1, 1992
Page 5

and surface water downgradient of the landfill may be natural subsurface material below the landfill as well as the material in the landfill itself.

The calculated risk provided in the Baseline Risk Assessment should also be considered in order to give a perspective on the importance of manganese as a contaminant of concern. The potential threat to human health from a site is calculated in terms of carcinogenic and noncarcinogenic risk. EPA has determined that the carcinogenic risk to people currently living, working or recreating on the site is unacceptable. Manganese is not classified as a carcinogen (Group D), and therefore does not contribute to this carcinogenic risk. Noncarcinogenic risk is evaluated by calculating the hazard index of an exposure pathway such as drinking groundwater. The hazard index is the sum of the hazard quotients of individual contaminants. For groundwater, the contribution of manganese to the hazard index is small. As shown on Table 5-29 of the BRA, the manganese contribution to the hazard index from ingestion of groundwater is less than or close to 1%. The hazard index for ingestion of surface water from Skinner Creek is much less than one (BRA Table 5-33); therefore, this surface water does not pose a noncarcinogenic health risk.

As a consequence, not only is permanganate only one of the possible sources of manganese in the environment (and permanganate would tend to immobilize rather than mobilize manganese), but manganese is not a very significant contributor to the calculated future risk of the site. In addition, the mobilization of manganese is likely due to other sources of contamination (organic waste) at the site which are affecting the subsurface redox conditions.

Sincerely,

WOODWARD-CLYDE CONSULTANTS



William J. Deutsch
Manager, Waste Engineering Services



Phyllis A. Brunner
Vice President